

AD-A212 111

(4)

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS DTIC FILE COPY		
2a. SECURITY CLASSIFICATION AUTHORITY SEP 08 1989		3. DISTRIBUTION/AVAILABILITY OF REPORT Unclassified/Unlimited		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report 15		
5a. NAME OF PERFORMING ORGANIZATION Dept. of Chem. Eng. & Mat. Sci. Corrosion Research Center		5b. OFFICE SYMBOL (if applicable)		5. MONITORING ORGANIZATION REPORT NUMBER(S)
6a. ADDRESS (City, State, and ZIP Code) University of Minnesota Minneapolis, MN 55455		7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION DARPA/ONR		8b. OFFICE SYMBOL (if applicable) Code 1113		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract No. N00014-88-K-0360
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.
		WORK UNIT ACCESSION NO.		
11. TITLE (Include Security Classification) Assessment of Thin Film Batteries Based on Polymer Electrolytes: 1. Energy Density				
12. PERSONAL AUTHOR(S) M.Z.A. Munshi, B.B. Owens				
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 7/88 TO 6/89		14. DATE OF REPORT (Year, Month, Day) 89/06/15
				15. PAGE COUNT 22
16. SUPPLEMENTARY NOTATION to be submitted to Solid State Ionics				
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The theoretical energy density performance limits for packaged rechargeable lithium polymer electrolyte batteries of both prismatic unipolar and bipolar electrode configurations are discussed. The electrolyte is based on complexes formed between polyethylene oxide and a lithium salt, and the composite cathode is V₆O₁₃. The modeling study suggests that specific energies up to 450 Wh/kg are possible for packaged batteries based on both unipolar and bipolar cell designs. This requires the use of low density metallic or metallized plastic current collectors. (AW)				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Boone B. Owens		22b. TELEPHONE (Include Area Code) (612) 625-1332		22c. OFFICE SYMBOL

ASSESSMENT OF THIN FILM BATTERIES BASED ON POLYMER ELECTROLYTES

I. Energy Density

M. Z. A. Munshi

B. B. Owens

Corrosion Research Center

Department of Chemical Engineering and Materials Science

University of Minnesota

Minneapolis, MN 55455

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Subject
A-1	



ABSTRACT

The theoretical energy density performance limits for packaged rechargeable lithium polymer electrolyte batteries of both prismatic unipolar and bipolar electrode configurations are discussed. The electrolyte is based on complexes formed between polyethylene oxide and a lithium salt, and the composite cathode is V_6O_{13} . The modeling study suggests that specific energies up to 450 Wh/kg are possible for packaged batteries based on both unipolar and bipolar cell designs. This requires the use of low density metallic or metallized plastic current collectors.

1.0 INTRODUCTION

Following the discovery of ionically conducting polymer electrolytes based on polyethylene oxide - alkali metal salt complexes [1] and the realization of rechargeable lithium solid state batteries utilizing such electrolytes [2], more recent battery development has focused on ambient temperature solid electrolytes with insertion cathodes such as TiS_2 or V_6O_{13} [3 - 5]. The

first such batteries had to operate near 100°C because of the poor conductivity of the solid polymer electrolyte at room temperature ($10^{-9} - 10^{-8} (\Omega\text{cm})^{-1}$) [6,7]. During the past 5 years, intense activity has centered mainly around the polymer electrolyte in an effort to develop alternative polymers with higher ionic conductivities at ambient temperatures [8 - 10]. Recently, a number of laboratories have reported ambient temperature operation for lithium polymer electrolyte batteries [11,12].

A number of advantages have been cited for solid state lithium polymer electrolyte batteries over other types of solid state batteries [13], including the good interfacial integrity critical to the overall performance of any solid state cell. The potential application for polymer electrolyte batteries span the entire range of battery products from smart credit cards to electric vehicle propulsion. Hence there is a need for both small and large area batteries and thick and thin film cells. A substantial amount of effort has been devoted to the characterization of polymer electrolytes as outlined in recent comprehensive review articles [11,14] but full cell studies have not been well documented. Only a few laboratories have reported the successful cycling of small prototype batteries based on lithium anodes, polymer electrolytes and insertion cathodes [4,5,11,15,16]. This has impeded the development of large scale cells. Despite this, the future prospects for this system remain high especially since the fabrication technology is relatively straightforward with automated techniques. In addition, the progress in the development of new polymer electrolytes with high ionic conductivities at ambient temperatures will open up a wider application range for the all solid state concept. Hence there is a greater need to investigate the effect of scale with respect to the energy and power capabilities.

Several important issues need to be addressed before cells reach the manufacturing stage. These include cost, fabrication techniques, long-term electrochemical behavior and ways in which cells are assembled to make batteries. Cells can be stacked in series or parallel arrangements to increase the voltage or current, respectively. One approach suggested by Harwell to reduce weight and cost during scale-up is to use bipolar modules [17]. A number of advantages and disadvantages are cited for bipolar and unipolar electrodes respectively [18]. The performance of a scaled-up battery (whether stacked in series and / or parallel arrangement) must be similar to small scale laboratory prototypes. It is important that new problems in either the

electrochemical performance or the fabrication techniques do not compromise the scale-up. For example, it is important that individual cells stacked in various arrays are well balanced in capacity in order to avoid over-charging or over-discharging. This is a critical issue since there apparently are no side reactions to provide a cell leveling mechanism in this system. Armand has suggested a tolerance level of 1 - 2% in the cell manufacture[19]. Other issues that need to be considered are thermal management and safety of large area series/parallel inter-connected cells. Finally the use of metallized plastic current collectors should bring the cost and weight down considerably, hence increasing the specific energy and power of the system.

Till recently there were two main groups that reported polymeric electrolyte battery scale-up. These are the groups at IREQ and Harwell. The Mead - H & L Engineering group (U.S.A. and Denmark) have recently described their ambient temperature battery, with quite good performance in terms of specific energy and power. IREQ (Canada) has built 10 Wh (operating at 95°C) and 1 Wh (operating at room temperature) cells, both of the flat-plate design [3,20]. The cells were of double cathode/central anode bi-cell construction and the overall conclusion was that no performance loss was experienced when the cell surface area was increased by a factor of 1000. More recently they have designed a 280 Wh battery. There has also been some consideration of spiral wound designs.

At Harwell (England), larger prototype (36 Wh, 8 Ah) batteries containing ten individual cells have been successfully built and cycled and their conclusion corresponds with that of IREQ in that cell area can be increased by 1000 times without significant loss in the electrochemical performance [14]. Without optimization the practical energy density including packaging, was estimated to be around 85 Wh/kg.

Larger batteries were designed about a prismatic bipolar unit. Twenty series connected bipolar units (plate area $20 \times 20 \text{ cm}^2$), were stacked further in 30 parallel units (total of 600 individual cells), and were modeled for the electric vehicle application. By making suitable allowances for the current collectors, bus-bars, terminals and other packaging materials, theoretical energy densities in excess of 400 Wh/kg were calculated. Practical energy densities of greater than 200 Wh/kg have been envisaged. In order to achieve optimum specific energy capabilities from large area cells, a bipolar configuration must be employed.

The primary goal of the present paper is to provide an overall assessment of the

optimum specific energy of a lithium polymer electrolyte battery that may be obtained by scale-up. Important parameters to consider for scale-up are the planar surface areas, thicknesses and densities of the cell components, number of bipolar units and capacity loading.

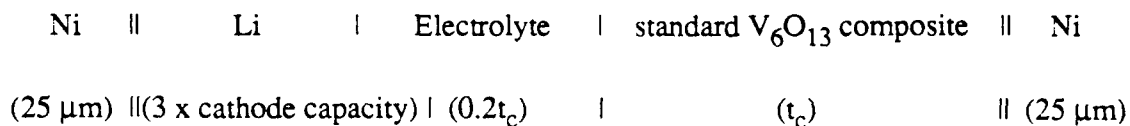
2.0 DESIGN CONCEPT

The approach involved macroscopic modeling of two design concepts:

- (1) prismatic unit cell
- (2) prismatic bipolar cells

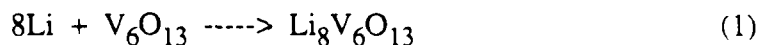
Figure 1 shows a schematic of a prismatic bipolar battery. The battery is reduced to a unit cell by the removal of the bipolar units.

In each case two types of current collectors are considered, (a) metallic and (b) metallized plastic. The unit cell was based on the following configuration, e.g., for Ni current collectors.



where t_c = the thickness of the cathode

The stoichiometric cell reaction[21] is assumed to be



Cathode thicknesses considered were 1, 10 and 100 μm and theoretical energy density values were calculated for square shaped prismatic cells with side dimensions ranging from 1 to 1000 cm.

The standard cathode composition was

75.4 w/o V_6O_{13}

5.0 w/o Carbon

19.6 w/o Electrolyte

and from a knowledge of the densities of the various cell components, the capacity factor per cm^3 (k_1) was calculated to be 0.849 Ah/cm^3 . This factor was used for all the cathode areas in order to deduce the cathode capacities.

The capacity for Li was calculated to equal 3 times the theoretical cathode capacity and the anode thicknesses were calculated accordingly for the appropriate thickness of cathode. The electrolyte was polyethylene oxide complexed with a lithium salt in the 8:1 O:Li ratio (conductivity assumed to be $10^{-4} (\Omega\text{cm})^{-1}$), although other electrolytes of similar conductivities could be substituted. The widths of the electrolyte and the current collector elements were 0.2 cm greater than the width of the electrodes. The spacer was 0.2 cm in width and occupied the perimeter of the cell, around the electrode. The thickness of the spacer was equal to the thickness of Li and cathode. The electrolyte thickness was 0.2 times the cathode thickness.

For the unit cell case, Ni current collectors (25 μm) were considered in one configuration and metallized (Ni) plastic current collectors in another. The thickness of the metallized layer was assumed to be 1000\AA on each side of the plastic (25 μm). Although it is possible that high resistive losses may be encountered across these metallized layers, the planar design concept of the plastic substrate could easily be converted to a microporous concept whereby the Ni would be deposited in a continuum.

For the bipolar design with metallic current collectors, Ni (25 μm) was considered for the end units and Al (15 μm) for the bipolar units. The Ni is assumed here in order to provide sufficient rigidity to the packaged battery.

In another case, 25 μm metallized (Ni $\sim 1000\text{\AA}$) plastic current collectors are assumed throughout the assembly.

For both bipolar cases, cathode thicknesses of 1, 10 and 100 μm and cell areas

from 1 cm^2 to 10^6 cm^2 were considered. From a knowledge of the cathode capacity, Q (Ah) and the weight w_1 (gm) of the unit cell components, the energy density of the unit cell was calculated using equation (2).

$$\text{Energy density} = Q (2.2) 1000 / w_1, \quad \text{Wh/kg} \quad (2)$$

which assumes an average cell output of 2.2 volts.

The energy density for the bipolar battery was calculated using equation (3)

$$\text{Energy density} = Q (2.2) (1 + x) 1000 / (w_1 + w_2 x), \quad \text{Wh/kg} \quad (3)$$

where w_2 is the weight of each bipolar unit and x is the number of bipolar units.

3.0 RESULTS AND DISCUSSION

3.1 Unit Cell

The energy density vs cell-area curves for the unit cell with Ni current collectors are shown in Figure 2 for 1, 10 and 100 μm thick cathodes. The specific energy increases with cathode thickness as expected. In addition, a plateau is reached in the specific energy for all three cathode thicknesses at around 1000 cm^2 cell area for the 1 μm cathode and 100 cm^2 cell area for 10 and 100 μm thick cathodes. The maximum specific energy occurs for the 100 μm thick cathode at a value of about 240 Wh/kg. A plot of specific energy vs cathode thickness for the Ni current collectors is shown in Figure 3 for t_c values out to 1000 μm . The figure also shows the energy density for the theoretical cell reaction, (1) and is compared to the reaction where the V_6O_{13} is a composite cathode consisting of V_6O_{13} , C and electrolyte phase, and also the reaction where threefold excess of Li is used with the composite cathode. The energy density for the packaged cell approaches a limiting value of about 450 Wh/kg with increasing cell thickness.

The corresponding energy density vs cell-area curves for the unit cell with

metallized plastic current collectors are shown in Figure 4 for 1, 10 and 100 μm thick cathodes. Again the specific energy increases with cell area and cathode thickness reaching a plateau at about 100 cm^2 . For the 10 and 100 μm thick cathode, the specific energy increases more steeply than for the 1 μm thick cathode. This is also true for the Ni current collector. The metallized plastic current collector appears to bring the weight of the battery down considerably in sharp contrast to the Ni current collector resulting in a doubling of the energy density ($\sim 460 \text{ Wh/kg}$) for the 100 μm thick cathode at 100 cm^2 cell area. Further increases in the area have little effect on the specific energy. This is true for every case considered.

A plot of specific energy vs cathode thickness for the metallized plastic current collectors is shown in Figure 5. In this case the energy density for the packaged cell approaches a limiting value of about 500 Wh/kg with increasing cell thickness.

A comparison of Figure 3 with that of Figure 5 suggests that, although ultimately comparable values of specific energies result for both Ni and metallized plastic current collector cells with large cathode thicknesses, the highest value of specific energy are realized with more efficient, thinner electrode structures in the case of the metallized plastic current collectors.

3.2 Bipolar Cells

The energy density vs number of bipolar units for cells with metallic current collectors are shown for 1, 10 and 100 μm thick cathodes as a function of cell area in Figures 6a, b and c respectively. The energy density reaches a limiting value with both the number of bipolar units and cell area and increases more steeply initially with increasing cathode thickness. The plateaus in the energy densities are reached more quickly with thicker cathodes. The optimum cell area appears to be between 400 cm^2 and 2500 cm^2 ; however, areas between 25 cm^2 and 100 cm^2 are also a good working range without too severe a penalty in the energy density. For the 100 μm thick cathode, the optimum number of bipolar units is about 20. For this number of units and a cell area of 400 cm^2 , an energy density of about 450 Wh/kg can be envisaged for 100 μm thick cathodes. This value compares well to the unit cell data using metallized plastic current collectors.

The energy density vs number of bipolar units for cells with metallized plastic current collectors are shown for 1, 10 and 100 μm thick cathodes as a function of cell area in

Figures 7a, b and c respectively. Again a flattening in the energy density takes place with the number of bipolar units and this occurs more steeply with increasing cathode thickness. The optimum area of the cell appears to be the same as that for the Ni current collector cells. The optimum specific energy of a battery with 100 μm thick cathodes consisting of about 5 bipolar units and a cell area of 400 cm^2 is calculated to be about 470 Wh/kg. Further increase in the cell area or the number of bipolar units has little effect on the energy density. Even with a 100 cm^2 area bipolar (5 units) cell battery, an energy density of 450 Wh/kg is envisaged.

The above results yield an upper limit for performance capability and are in excellent agreement with the work of Hooper[14,17]. Figure 8 summarizes the specific energy of a lithium/metal oxide polymer electrolyte cell system with a state-of-the-art lithium/liquid electrolyte battery. The battery electrode couple $\text{Li}/\text{V}_6\text{O}_{13}$ has a very high theoretical specific energy in excess of 800 Wh/kg. This value is reduced to 650 Wh/kg by practical electrode design constraints. Further energy reduction results from the necessary inclusion of hardware, including insulators, current collectors and battery cans. Finally, allowing for less than 100% cathode utilization, the projected available energy of 200 - 300 Wh/kg still represents a 100% increase in specific energy vs that of state-of-art lithium rechargeable batteries and a three to five fold increase relative to established secondary batteries. At very low current drains, one could get close to the theoretical energy density. However, most battery systems operate at the C to C/10 rates of discharge and in these cases, 40-60% of cathode utilization is not unreasonable to assume[5]. Experimental studies on small laboratory unit cells (1 - 6 cm^2 area) show that these batteries now provide an energy capacity of up to 200 Wh/kg.

4.0 CONCLUSIONS

In order to increase the specific energy of a polymer electrolyte battery, one needs to employ a bipolar plate design. The use of a metallized plastic current collector is expected to decrease not only the weight and the cost, but also to increase the specific energy of the system considerably. For the unit cell, optimum specific energies of 240 Wh/kg are calculated for cells with Ni current collectors, 100 μm thick cathode and 100 cm^2 cell areas, whereas for the

metallized plastic current collector, 460 Wh/kg are calculated for a 100 μm thick cathode with the same cell area.

Further small increases in the energy densities are obtained using a bipolar configuration. Optimum specific energies of about 450 Wh/kg are obtained for cells using an Al current collector with 20 bipolar units, 400 cm^2 cell area and 100 μm thick cathode. This means one can use lightweight metal current collectors but in a bipolar configuration in order to achieve similar energy densities to that of a metallized plastic current collector in a unit cell.

The use of metallized plastic current collector gives optimum specific energies of about 470 Wh/kg for cells with 5 bipolar units, 100 μm thick cathode and 400 cm^2 cell areas. This does not represent a very large increase over the Al current collector in a bipolar configuration nor the unit cell values using a metallized plastic current collector. However, for the bipolar case, the number of units are much lower as compared to the Al current collector.

In almost all cases, the optimum cell areas range between 100 cm^2 - 400 cm^2 . Further increase in the area does not have a great impact in increasing the specific energy. Overall, the maximum energy density available, whether it be for unit or bipolar cells using metallized plastic current collector or bipolar Al current collector cells, is about 470 Wh/kg. Practical energy densities of about 200 - 300 Wh/kg are achieved with further development.

ACKNOWLEDGEMENT

This work was sponsored in part by the Office of Naval Research and the Defense Advanced Research Projects Agency.

REFERENCES

- [1]. B. E. Fenton, J. M. Parker and P. V. Wright, Polymer 14, (1973) 589.
- [2]. M. Armand, J. M. Chabagno and M. Duclot, in: Fast ion transport in solid, eds. P. Vashista, J. N. Mundy and G. K. Shenoy (North-Holland, Amsterdam, 1979) 131.
- [3]. M. Gauthier, 1st Int'l Symposium on Polymer Electrolytes, St. Andrews, Scotland, (1987).

- [4]. A. Hooper and J. M. North, *Solid State Ionics*, 9/10, 1161 (1983).
- [5]. M. Z. A. Munshi and B. B. Owens, *ibid.* 26,41 (1988).
- [6]. C. D. Robitaille and D. Fauteux, *J. Electrochem. Soc.*, 133, 315 (1986).
- [7]. M. Z. A. Munshi and B. B. Owens, in: *Superionic solids and solid electrolytes*, eds. A. Lasker and S. Chandra (Academic Press, 1989).
- [8]. M. L. Kaplan, E. A. Reitman, R. J. Cava, L. K. Holt and E. A. Chandross, *Solid State Ionics*, 25, (1987) 37.
- [9]. P. M. Blonsky, D. F. Shriver, P. Austin and H. R. Allcock, *ibid.* 18/19, (1986) 258.
- [10]. M. Watanabe and N. Ogata, in: *Polymer electrolyte reviews 1*, eds. J. R. MacCallum and C. A. Vincent (Elsevier Applied Science, London, 1987) 39.
- [11]. M. Gauthier, A. Belanger, B. Kupfer, G. Vassort and M. Armand, in: *Polymer electrolyte reviews 2*, eds. J. R. MacCallum and C. A. Vincent (Elsevier Applied Science, London, 1989).
- [12]. D. Shackles, *Fourth Int'l Seminar on Lithium Battery Technology and Applications*, Mar. 6-8, Deerfield Beach, FL (1989).
- [13]. M. Z. A. Munshi and B. B. Owens, *IEEE Spectrum*, 26(8), (1989) 32.
- [14]. A. Hooper, in: *Materials and processes for lithium batteries*, eds. K. M. Abraham and B. B. Owens, (The Electrochemical Soc., Inc., NJ, 1989) 15.
- [15]. K. W. Semkow and A. F. Sammells, *J. Electrochem. Soc.*, 134, (1987) 767.
- [16]. K. M. Abraham, M. Alamgir and S. J. Perotti, *ibid.*, 135, (1988) 535.
- [17]. R. M. Dell, A. Hooper, J. Jenson, T. L. Markin and F. Rasmussen, in: *Advanced Batteries and Fuel Cells*, EUR 8660 EN, (1983).
- [18]. M. Z. A. Munshi and B. B. Owens, "Assessment of Thin Film Batteries Based on Polymer Electrolytes, II - Pulse Power Density Variation", *this journal*.
- [19]. M. B. Armand, J. M. Chabagno and M. Duclot, *2nd Int'l Conf. on Solid Electrolytes*, St. Andrews, Scotland (1978), Ext. Abstracts.
- [20]. M. Gauthier, M. Armand and D. Muller, in: *Electroresponsive Molecular and Polymer Systems*, ed. T. A. Skotheim, (Marcel Dekker, Inc. N.Y., 1988) 41.
- [21]. D. W. Murphy and P. A. Christian, *Science*, 205 (1979) 651.

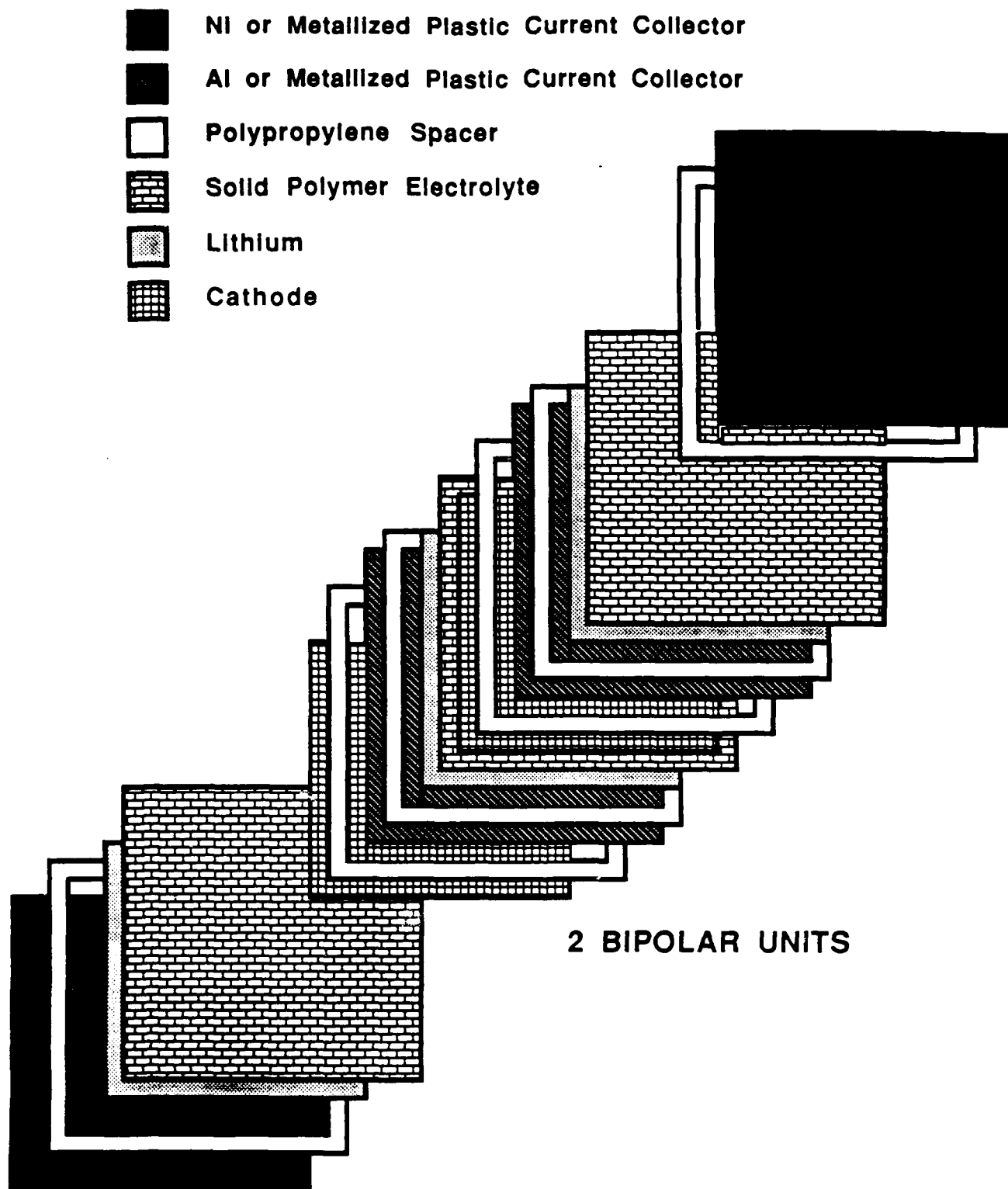


Figure 1. Schematic of a prismatic bipolar (2 units) battery.

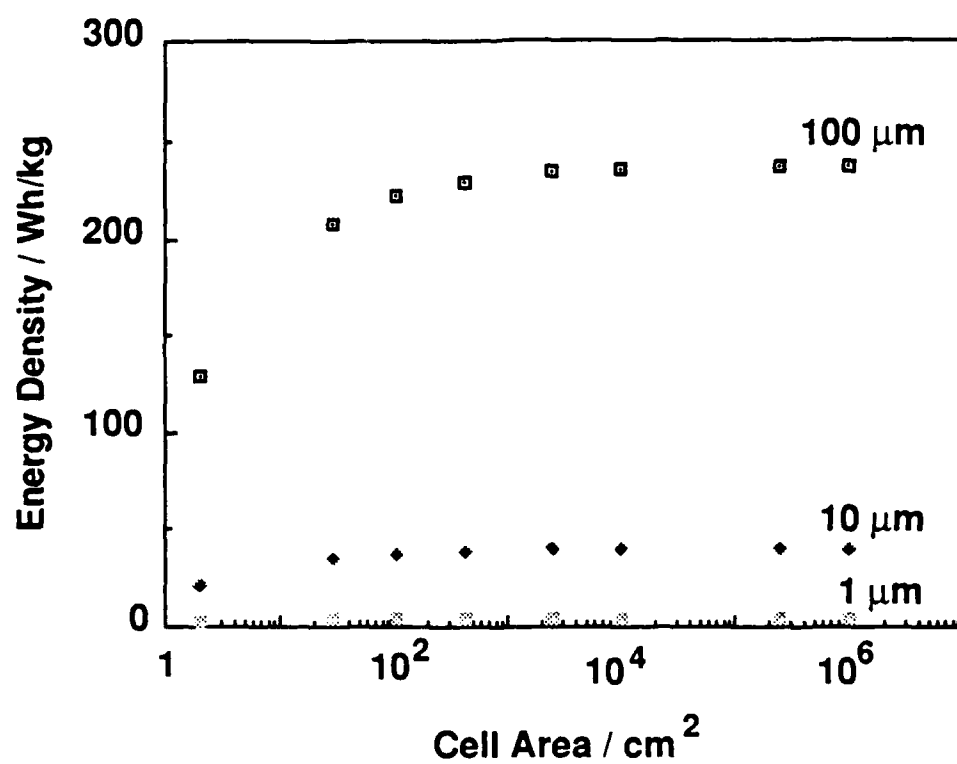


Figure 2. Energy density versus cell-area for Ni current collector unit cell, with 1, 10 and 100 μm thick cathode.

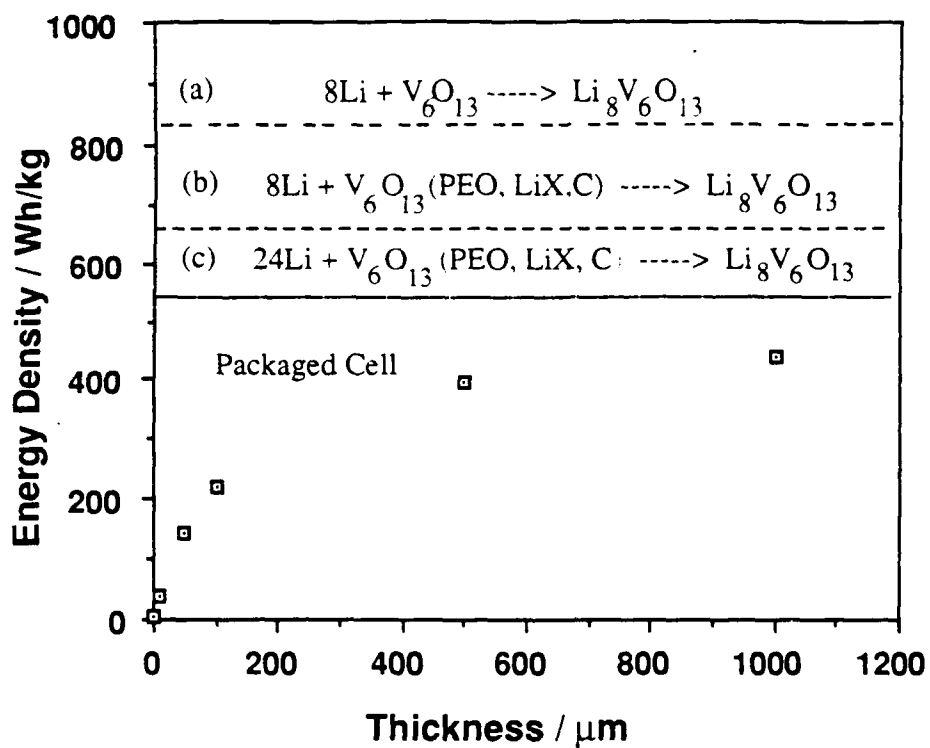


Fig. 3. Specific energy vs cathode thickness for 100 cm^2 unit cell with Ni current collector are compared to the theoretical values for (a) balanced electrodes; (b) same as (a), including non-electroactive cathode additives; (c) same as (b), including excess Li.

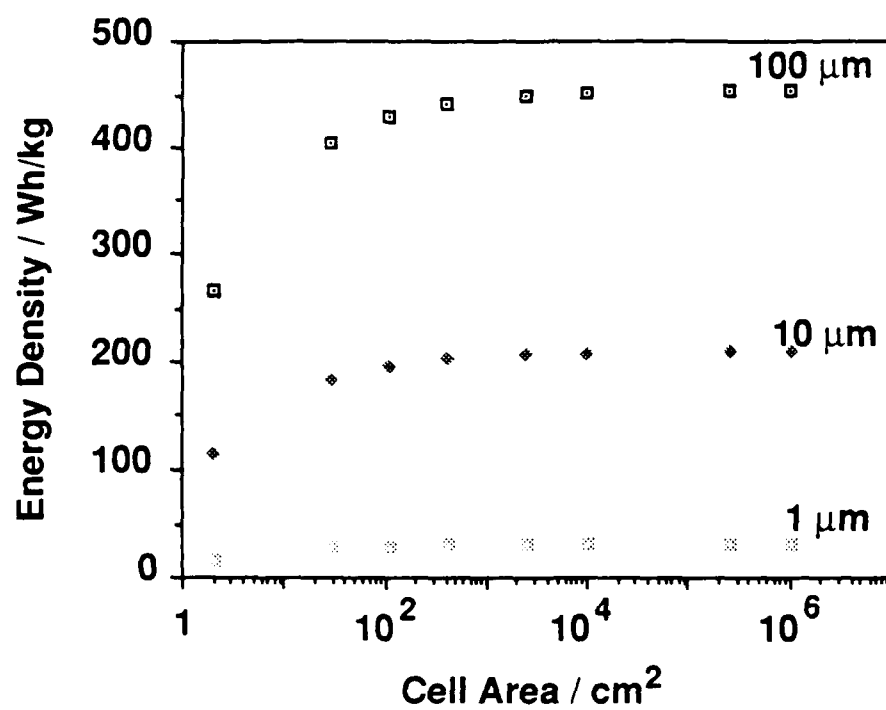


Figure 4. Energy density versus cell-area for metallized plastic current collector unit cell with 1, 10 and 100 μm thick cathodes

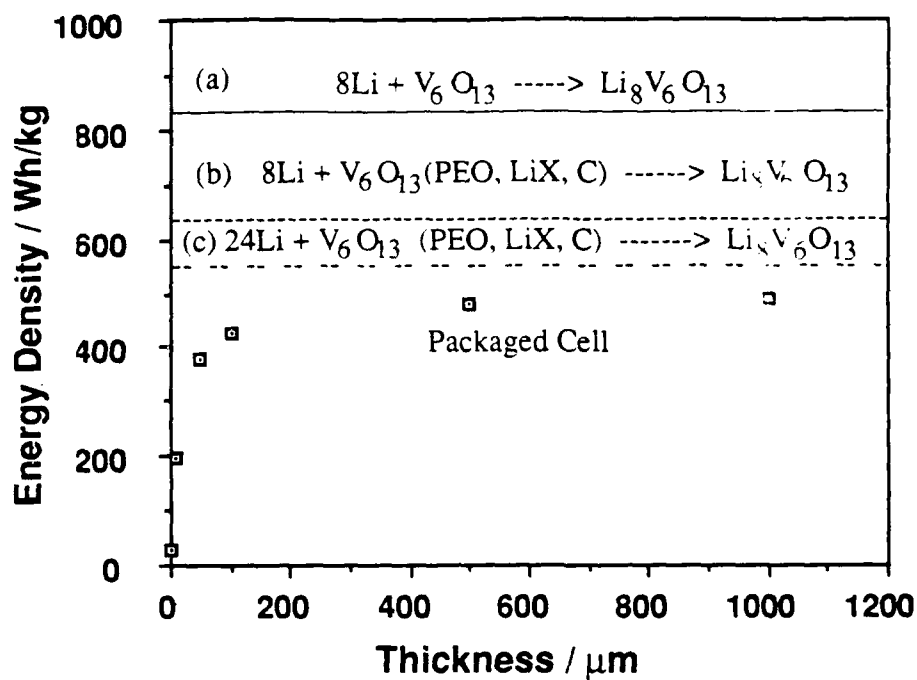


Fig. 5. Specific energy vs cathode thickness for 100 cm^2 unit cell with metallized plastic current collector are compared to the theoretical values for (a) balanced electrodes; (b) same as (a), including non-electroactive cathode additives; (c) same as (b), including excess Li.

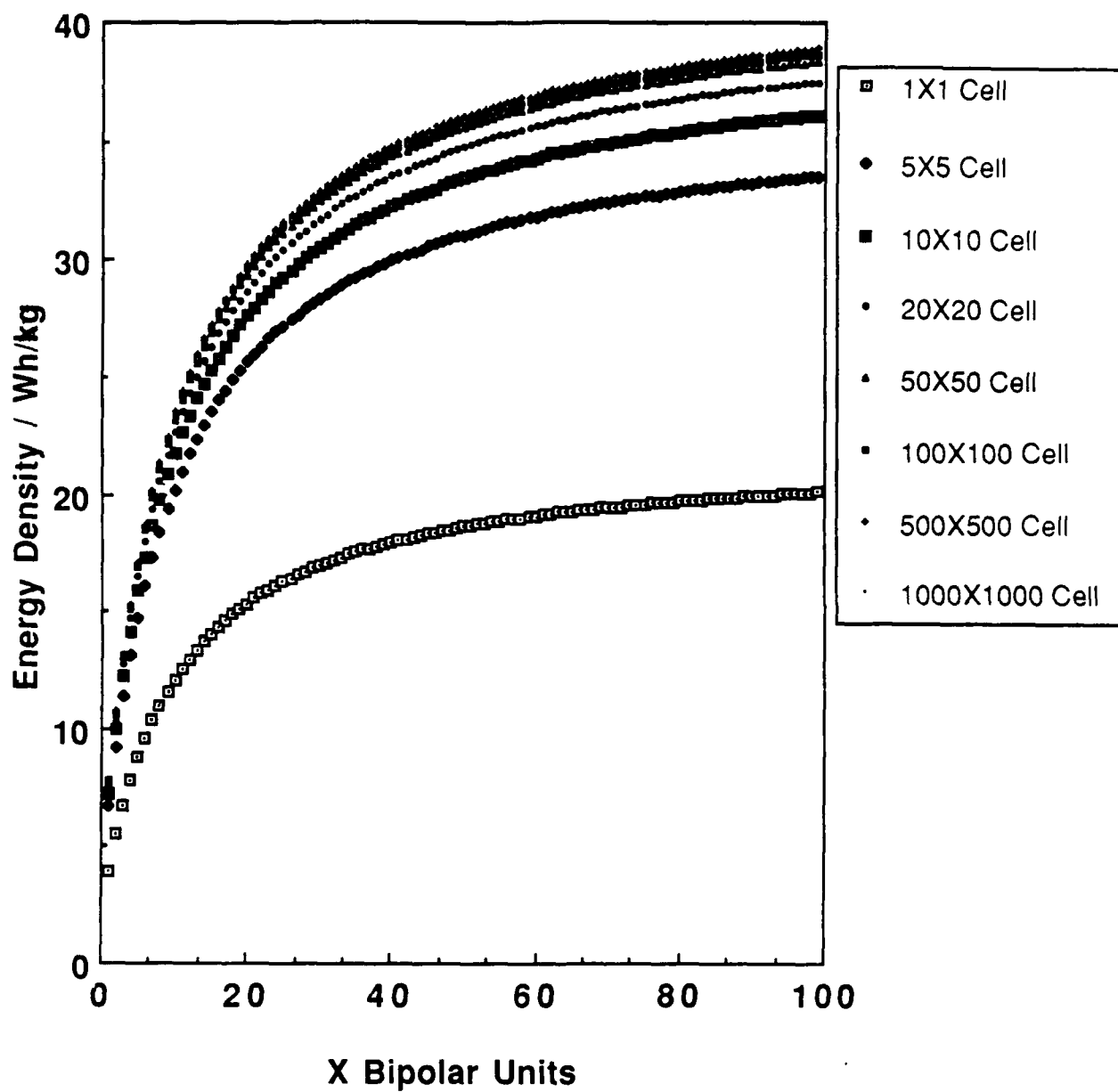


Fig. 6a. Energy density vs No. of bipolar units using Al current collector and 1 μ m thick cathode.

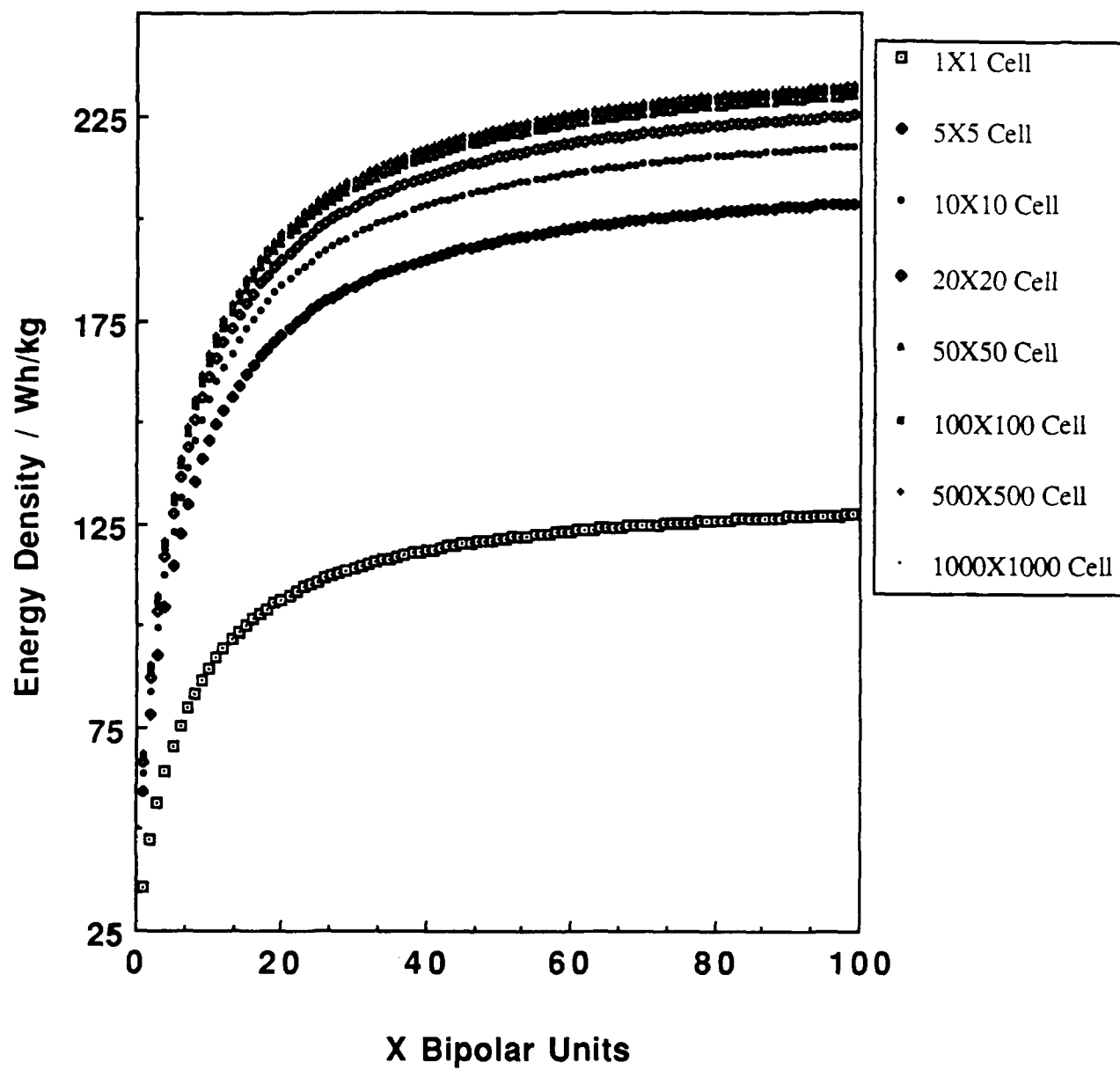


Fig. 6b. Energy density vs No. of bipolar units using Al current collector and 10 μ m thick cathode.

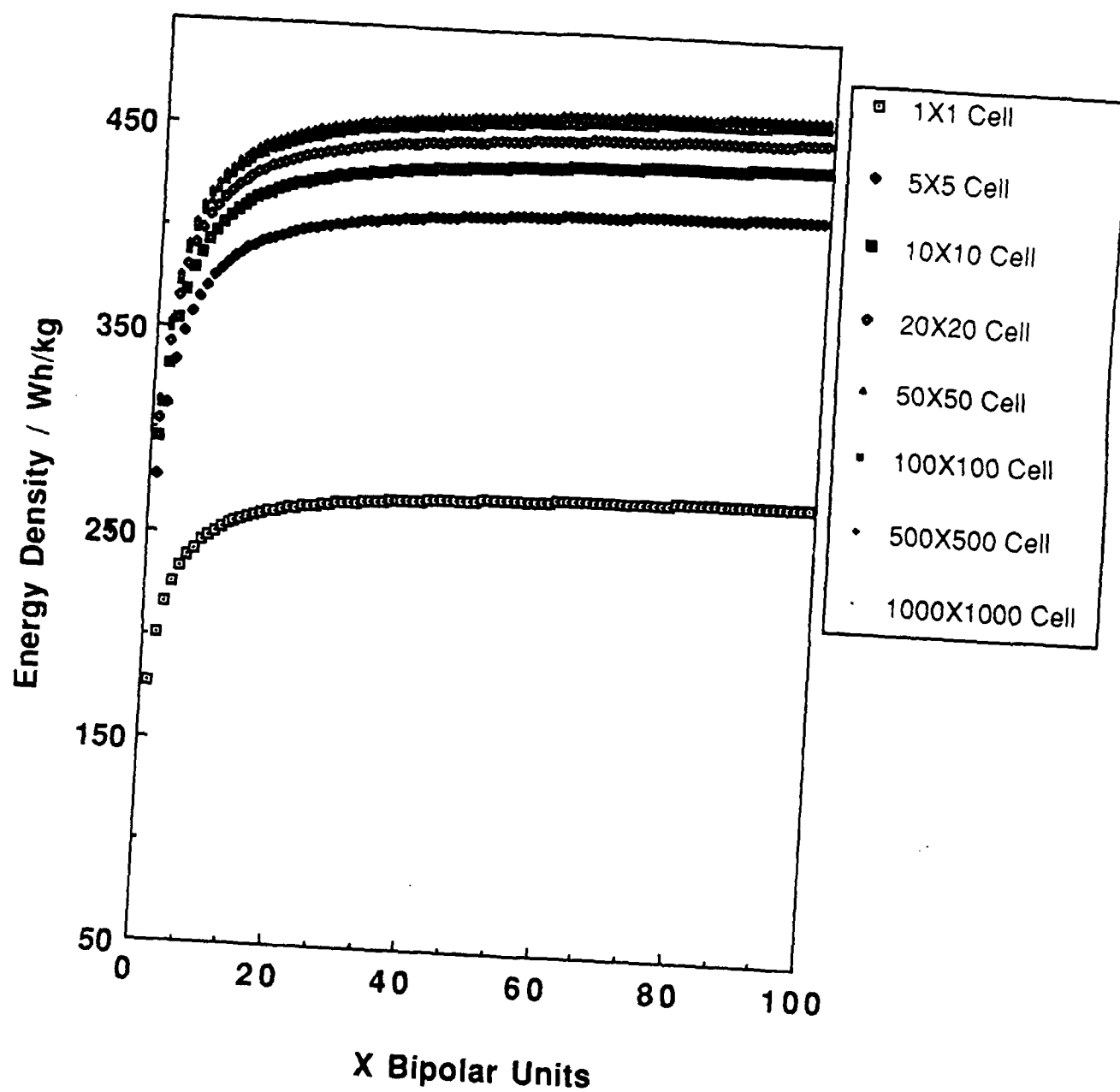


Fig. 6c. Energy density vs No. of bipolar units using Al current collector and 100 μ m thick cathode.

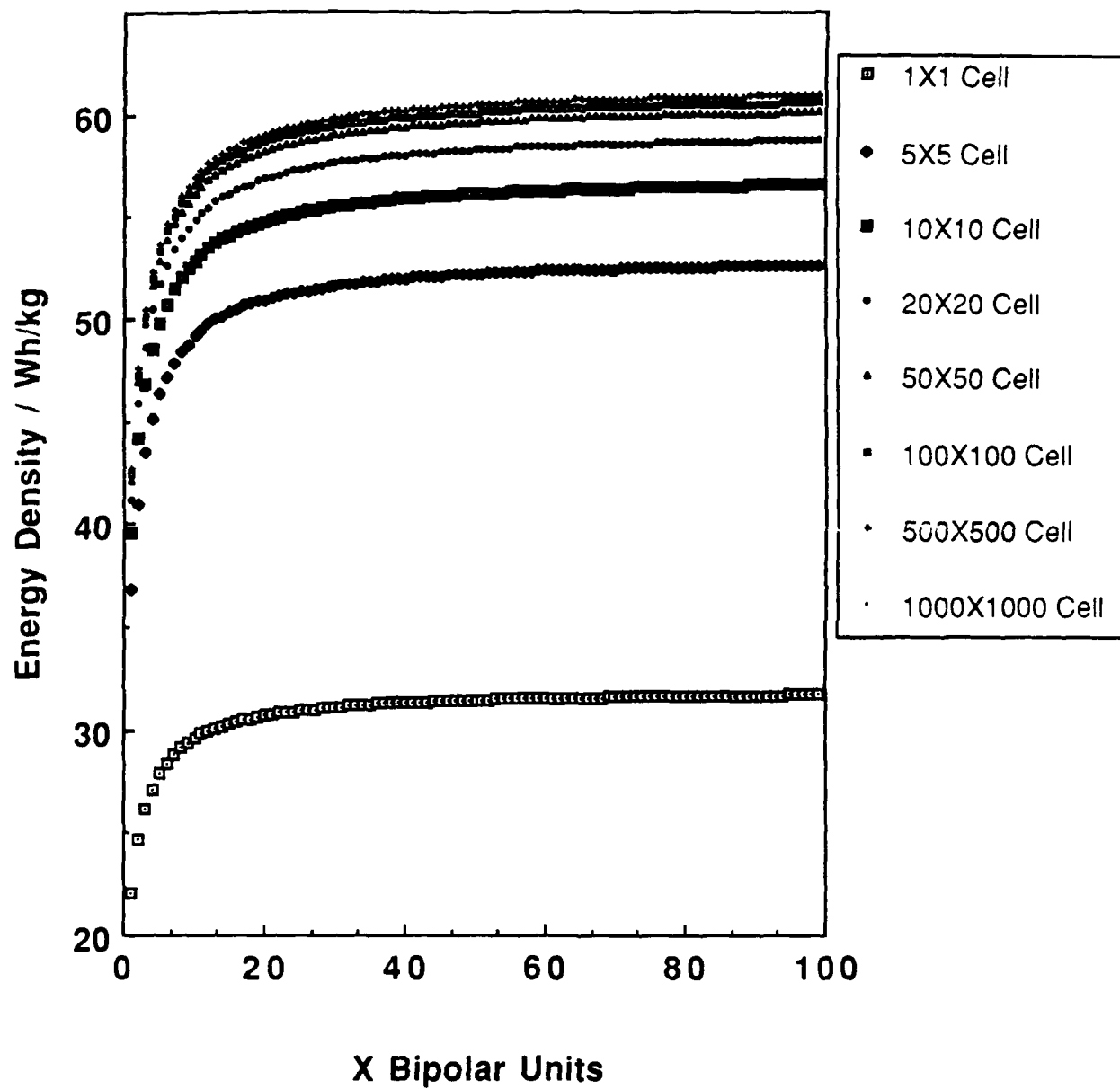


Fig. 7a. Energy density vs No. of bipolar units using metallized plastic current collector and 1 μm thick cathode.

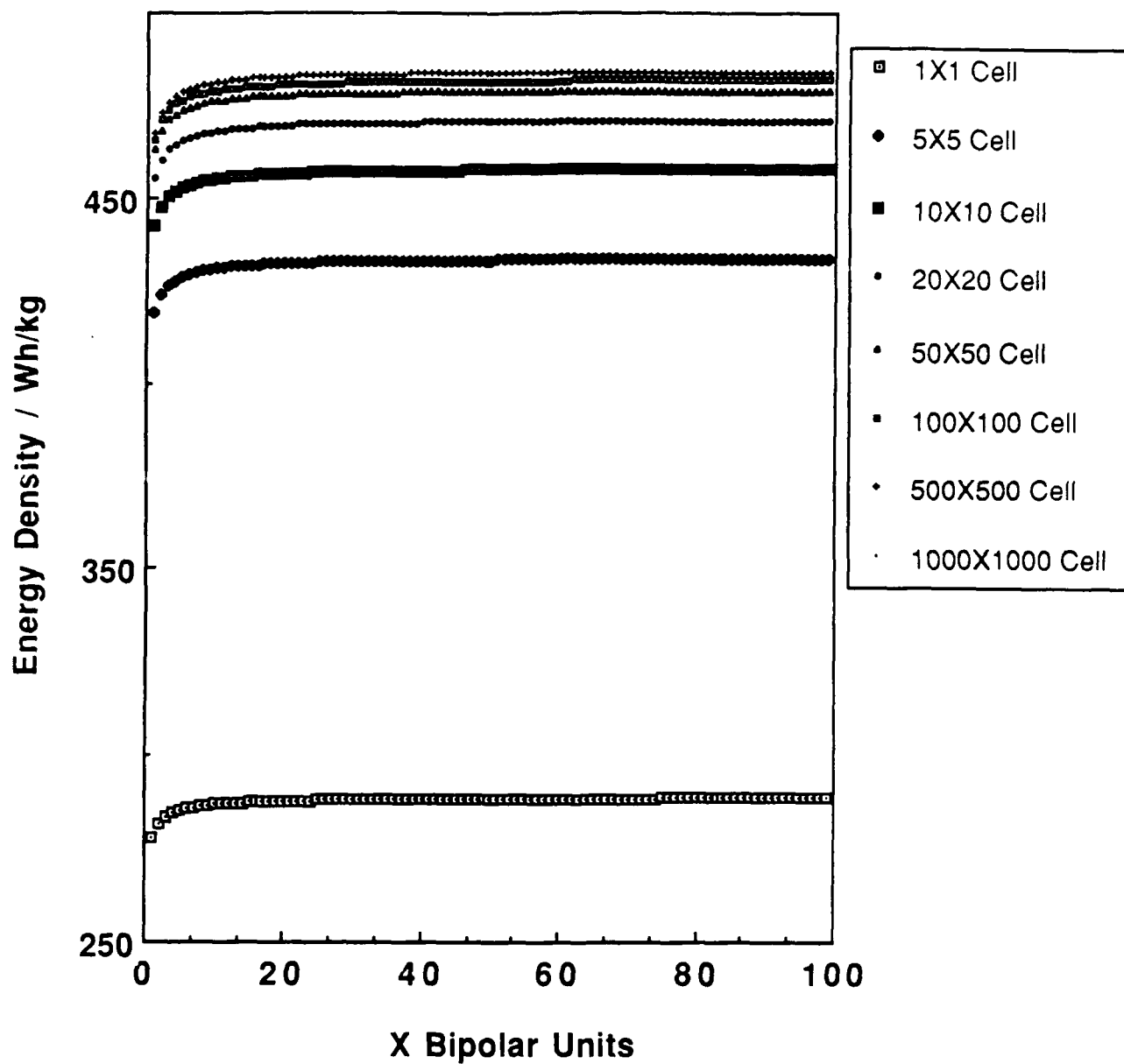


Fig. 7c. Energy density vs No. of bipolar units using metallized plastic current collector and 100 μ m thick cathode.

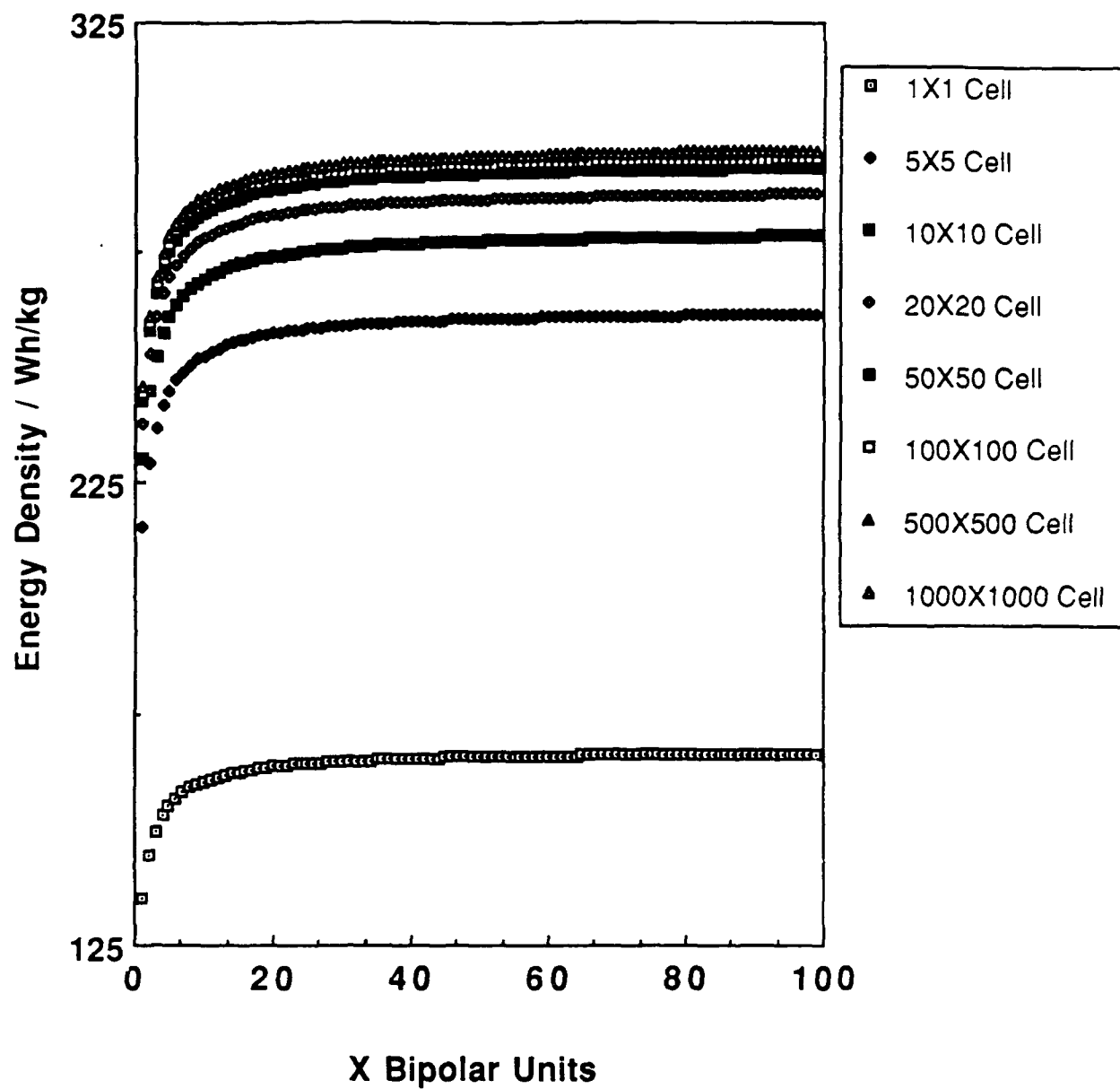


Figure 7b. Energy density vs No. of bipolar units using metallized plastic current collector and 10 μm thick cathode

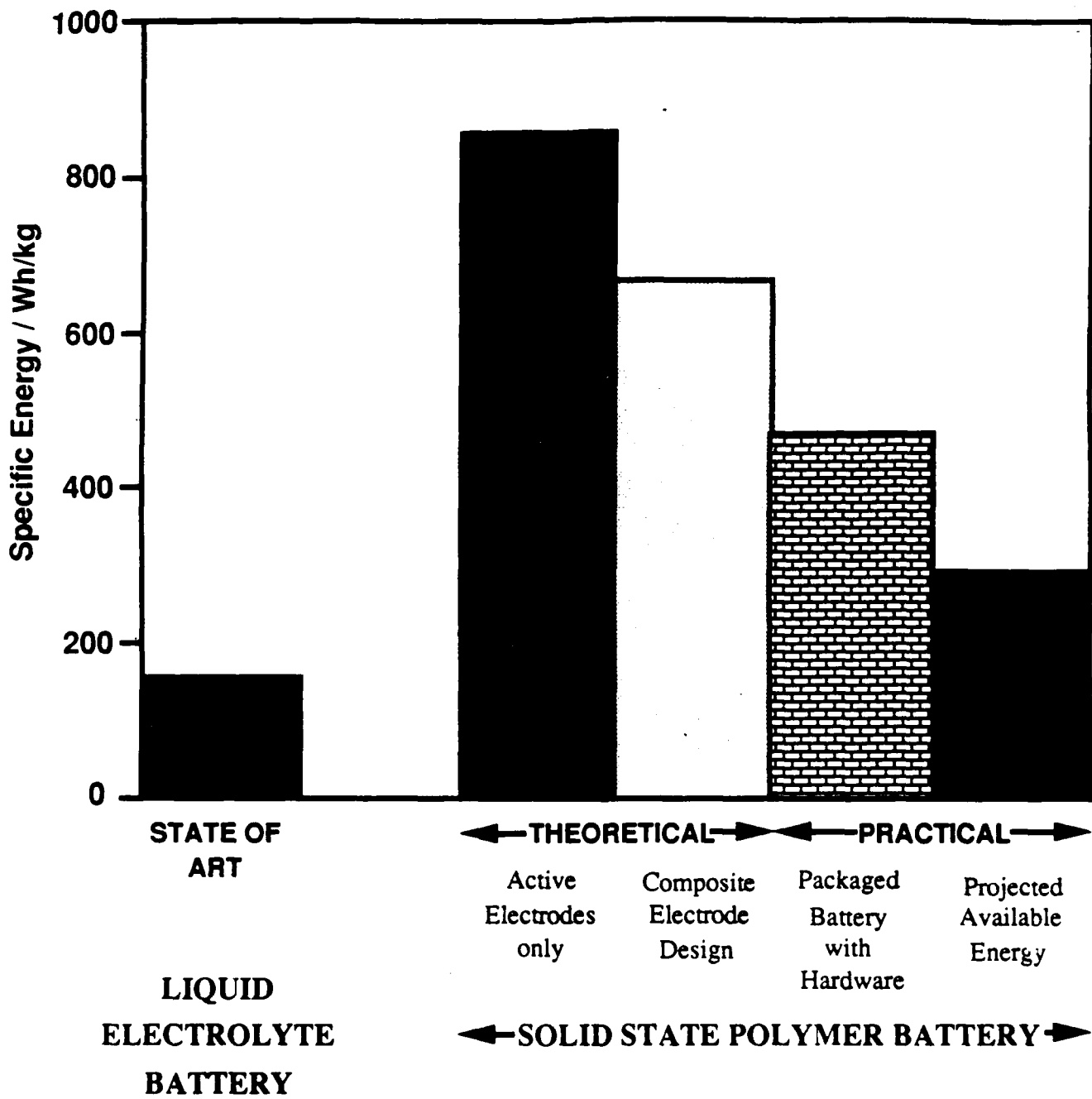


Figure 8. Specific energy of lithium batteries.